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BIOCOMPOSITES**

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Review

## VISCOELASTIC AND THERMAL PROPERTIES OF WOVEN SISAL FABRIC REINFORCED NATURAL RUBBER BIOCOMPOSITES

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### **Abstract**

Textile- rubber biocomposites were prepared by reinforcing natural rubber with woven sisal fabric. The viscoelastic properties of the composites were analysed at different frequencies. Sisal fabric was subjected to different chemical modifications like mercerization, silanation and thermal treatment and their influence on dynamic mechanical properties were analysed. Storage modulus was found to increase upon reinforcement of natural rubber with woven sisal fabric. Chemical modification of sisal fabric resulted in a decrease of storage modulus. The damping factor was found to decrease with chemical treatment and the gum compound exhibited maximum damping characteristics. Thermal stability of the composites were also analyzed by thermogravimetric studies. Scanning electron microscopic studies were performed to evaluate the morphology of fabric-matrix interface.

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## 1. INTRODUCTION

Developments in composite technology have encouraged rapid progress in natural fiber reinforced composites such as lignocellulosic composites. In this branch of science and technology, lignocellulosic fibers are especially important because of their lower specific gravity and easier processability compared to many other natural and synthetic fibers. Lignocellulosic fiber reinforced polymer composites are also attractively light weight. Applications of plant fiber reinforced composites are numerous ranging from consumer needs to engineering industries. Besides the development in textile technologies such as weaving, knitting and braiding has resulted in the formation of textile composites that have superior mechanical properties, as no discontinuous orientation of fibers is entailed at any point.

Dynamic mechanical properties of a composite material depend on the fiber content, presence of the additives like filler, compatibiliser, fiber orientation and the mode of testing. The three important parameters that can be obtained during a dynamic mechanical analysis are: (i) Storage modulus, which is a measure of the maximum energy, stored in the material during one cycle of oscillation ; this gives an idea of stiffness behavior and load bearing capability of composite material, (ii) loss modulus which is proportional to the amount of energy that has been dissipated as heat by the sample and (iii) the mechanical damping term  $\tan \delta$ , which is the ratio of the loss modulus to storage modulus and is proportional to the degree of molecular mobility in the polymer material<sup>1</sup>.

Donnell et al.<sup>2</sup> characterized the dynamic mechanical properties of natural fiber reinforced and acrylated epoxidized soyabean oil resin composites which were manufactured by vacuum assisted resin transfer moulding. The different natural fibers used were flax, hemp, cellulose and recycled newspaper. The authors observed that recycled newspaper reinforced resin composites exhibited a storage modulus value that was almost five times greater than that of the resin. The composites were also found to possess high damping characteristics making them a probable choice as material for anti-vibration parts in automotive industry.

The effect of alkali treatment on the dynamic mechanical properties of kenaf and hemp fiber reinforced polyester composites was analyzed by Aziz et al.<sup>3</sup>. The authors observed that the mechanical properties of a treated fiber composites have higher storage modulus values and lower damping parameter indicating greater interfacial bond strength and adhesion between the polyester resin matrix and the fiber and inferior impact properties compared to the untreated fiber composites. They have also noticed a similar pattern of result when cashew nut shell liquid is used as matrix<sup>4</sup>.

In an interesting study, Guigo et al<sup>5</sup>. analyzed the viscoelastic properties of green nanocomposites based on silicate/clays/lignin/natural fibres. They observed that the use of organophilic MMT resulted in a higher Tg and enhanced thermal stability. The properties of man made cellulose and abaca fibres were investigated by Bledzki et al<sup>6</sup>. The storage modulus of PLA-based composites was found to be much higher than of unreinforced PLA due to better stress transfer in the reinforced composites. The glass transition temperature derived from loss modulus shifted to higher temperatures, compared to matrix polymer.

In a study concerning hybrid bio-fiber systems, the dynamic mechanical properties of sisal-oil palm hybrid fiber reinforced natural rubber composites was analyzed by Jacob et al.<sup>7</sup> The authors noticed that there was an increase of storage modulus with fiber reinforcement while damping characteristics registered a decrease. Chemical modification of sisal and oil palm fibers resulted in an increase of storage modulus.

As described above it is evident that a number of investigations have been carried out on short fiber reinforced composites. Nevertheless, the viscoelastic and thermal properties of textile rubber composites have not been attempted till date. This study explores the dynamic mechanical behavior of woven sisal fabric reinforced natural rubber composites. The influence of chemical modification on the viscoelastic properties has also been determined. Moreover, the effect of frequency on the viscoelastic properties of the textile composites has also been examined.

## 2. EXPERIMENTAL

### 2.1 MATERIALS

Sisal fabric was obtained from local sources. Natural rubber used for the study was procured from Rubber Research Institute of India, Kottayam. The other ingredients used to vulcanize natural rubber were zinc oxide, stearic acid, 2, 2, 4-trimethyl-1,2-dihydroquinoline (TDQ), N-cyclohexylbenzothiazyl sulphenamide (CBS) and sulphur and was obtained from local rubber chemicals suppliers. Sisal fabric used in this study had a unidirectional type of fabric weave having a count of 20 (See Figure 1). The properties of woven sisal fabric are given in Table I.

### 2.3 FABRICATION OF COMPOSITES

Natural rubber was masticated on the mill for 2 minutes followed by addition of the ingredients. The rubber sheet was prepared in a laboratory two-roll mill (150 x 300mm). The nip-gap, mill roll, speed ratio, and the number of passes were kept the same for all the mixes. The bonding system consisting of resorcinol and hexamethylene tetramine was also incorporated. The sisal fabric – natural rubber textile composites (having a thickness of 3mm) were prepared by sandwiching a single layer of sisal fabric between two layers of pre-weighed rubber sheets which was then compression moulded at 150° C under a pressure of 120 bar for 8 minutes [See Figure 2]. The formulation of different composites is given in Table II.

### 2.4. CHEMICAL MODIFICATION OF SISAL FABRIC

The different chemical modifications performed were as follows:

#### *[a] ALKALI TREATMENT*

Sisal fabric was treated for 1 hour with NaOH solution of concentration 4 %. The fabric was further washed with water containing acetic acid. Finally the fabric was washed again with fresh water and dried in an oven.

#### *[b] SILANE TREATMENT*

The silane coupling agents used were Silane A1100 [3-aminopropyl tri-ethoxy silane] and Silane A174 [ $\gamma$ -Metharyloxypropyltrimethoxysilane]. 0.4% silane solution was

prepared by mixing 4g of respective silanes in ethanol (600ml) / water (400ml) mixture and was allowed to stand for 1 hour. The pH of the solution was maintained at 4 with the addition of acetic acid. Sisal fabric was dipped in this solution and was allowed to stand for 1.5 hours. The ethanol / water mixture was drained out and the fabric was dried in air and then in an oven at 70°C until it was completely dry.

### ***[c] THERMAL TREATMENT***

Thermal treatment was carried out by keeping the woven sisal fabric in the oven for 8 hours at 150°C. The fabric, directly from the oven was used for composite preparation.

### **2.5 MEASUREMENTS**

DMA measurements were carried out on Universal V2.6D TA Instruments. The test specimen was clamped between the ends of two parallel arms, which are mounted on low force flexure pivots restricting the motion only in horizontal plane. The samples were measured at operating frequencies of 0.1, 1 and 10 Hz and a heating rate of 2°C / min. The samples were evaluated in the temperature range from -100°C to +150°C.

Thermogravimetric analysis of the fabric reinforced composites was carried out by using a Universal V2.3C TA Instrument with temperature programmed at 20°C / min heating rate, from room temperature to 700 °C in presence of nitrogen gas having a flow rate of 20ml/min.

Scanning electron microscopic studies were conducted using JEOL, JSM 5800 to analyze the fracture behavior of the composites. The fracture ends of the tensile specimens were mounted on aluminium stubs and gold coated to avoid electrical charging during examination.

### 3. RESULTS AND DISCUSSION

#### 3.1 Viscoelastic properties

##### 3.1.1 Storage Modulus

Storage modulus provides valuable insight into the stiffness of a material with reference to temperature. It measures the elastic response of a material. Figure 3 shows the variation of storage modulus with temperature of the gum, untreated and treated samples at a frequency of 1 Hz. It can be seen that the composite containing untreated sisal fabric exhibits an increase in storage modulus as compared to the gum compound. Storage modulus mainly depends upon stiffness and rigidity of a composite. Any factor that increases the stiffness of the system will result in an increase of storage modulus. The gum compound comprising of only the rubber phase gives the material more flexibility resulting in a low degree of stiffness and hence low storage modulus. When sisal fabric (which is tightly knit) is incorporated in the otherwise flexible rubber matrix the stiffness of the composite increases resulting in high storage modulus. Also the addition of woven fabric allows greater stress transfer at the interface, which consequently increases the storage modulus.

It can also be observed that chemical modification of sisal fabric has resulted in a decrease of storage modulus. The mechanics of textile composites is different from that of short fiber composites. Generally it has been seen that chemical treatments increase the properties of the composite. In fact we have seen that the incorporation of mercerized sisal and oil palm fibers increased the tensile strength of natural rubber composites<sup>8</sup>. The major contribution to strength in textile composites is the alignment of yarns in warp and weft direction. Chemical treatment results in the partial unwinding of yarns (as hemicellulose dissolves off) and hence the alignment gets antagonized. This results in lowering of strength of composites. Another reason is that as sisal fabric is composed of thick strands and knots, the alkali and silane coupling agents did not penetrate into the fabric and therefore the interfacial properties between the sisal fabric and rubber matrix has not been improved enough. Hence, chemical treatment was ineffective due to which the high stiffness obtained in the former case was antagonized when the fabric was subjected to conventional chemical treatment of fibers.

Among the treated composites, composite containing silane (A174) treated fabric exhibits the highest storage modulus. This could be attributed to increased adhesion in these composites. The interfacial adhesion in chemically modified textile composites can be further understood by looking into fracture topography of the system. Scanning electron microscopy (SEM) is a useful method to analyze the degree of fiber/ matrix adhesion. Figure 4 a,b,c,d,e and f presents the tensile fracture surfaces of the untreated and various chemically modified composites. In Fig 4 (a) we can see the presence of cavities. This is due to the fact that individual strands of fiber are pulled out of the rubber matrix upon the application of stress. This indicates that the adhesion between rubber matrix and sisal fabric is not satisfactory in the absence of a bonding agent or chemical modification. Figure 4 (b) exhibits the SEM of the composite in presence of a bonding agent. Here there is a clear evidence of fiber breakage. The strong bonding between fabric and rubber matrix results in fibers being broken off rather than unwinding itself from the matrix. We clearly see broken ends of fibers being protruding from the matrix. Figure 4 (c) shows the SEM of tensile fracture surface of composite containing alkali treated sisal fabric. Generally mercerization treatment results in removal of lignin and hemicellulose; for this to take place it is essential that alkali penetrates each and every nook of the fabric. In this particular study we can see from the SEM that this has not occurred. This is because the woven sisal fabric is composed of thick yarns and when it is subjected to mercerization the alkali does not penetrate within the individual fiber strands. As a result the bonding is not uniform and effective. Hence composites prepared from the alkali treated fabric show impaired properties.

The SEM of tensile fracture surfaces of composites containing silane treated fabric is presented in Figure 4 (d & e). The individual strands of the fabric are seen to have a smoother appearance. The silanyl groups from the silane coupling agent promote better interaction between rubber matrix and fabric (Fig. 4 d). In Figure 4 (e) there is the presence of fiber breakage suggesting good bonding. Traces of silanyl coupling agent can be seen to adhere to the strands of the fabric surface. In Figure 4 (f) one can see the broken ends of fiber projecting from the matrix indicating a strong interface. Upon thermal treatment the hydrophilic nature of fibers decreases while the crystallinity of



fiber increases. As a result the adhesion between rubber matrix and sisal fabric increases giving rise to stronger interface as seen in the figure. Therefore we can state that there is no fiber pull out if the composites are thermally treated.

### 3.1.2 Loss modulus and damping characteristics

The loss modulus represents the viscous response of a material. Figures 5 present the variation of loss modulus with temperature as a function of chemical modification. It can be observed that maximum loss modulus is exhibited by the composite containing untreated sisal fabric and upon chemical modification the loss modulus value decreases. The height and area of the peak regions are also indications of the energy absorbed by the system. Compared to the untreated composite the peak height decreases for the composites comprising of chemically modified sisal fabric.

Damping is an important parameter related to the study of dynamic behaviour of fiber reinforced composite structures.  $\tan \delta$  relates to the impact resistance of the material. As the damping peak occurs in the region of the glass transition where the material changes from a rigid to a more rubbery state, it is associated with the segmental mobility within the polymer structure all of which are initially frozen in. Therefore higher the  $\tan \delta$  peak value, greater is the degree of molecular mobility<sup>1</sup>.

Figure 6 presents the variation of  $\tan \delta$  with temperature of the textile composites. It is observed that the gum compound exhibits maximum damping characteristics and damping decreases upon reinforcement with sisal fabric. Incorporation of fabric resulted in barriers being formed restricting the mobility of rubber chains, leading to lower flexibility, lower degrees of molecular motion and hence lower damping characteristics. Another reason for the decrease is that there is less matrix by volume to dissipate the mechanical energy. When compared to the untreated composite, one can see that chemically modified composites exhibit lower damping characteristics.

Table III presents the  $T_g$  values from loss modulus peak and  $\tan \delta$  peak. It is evident that the incorporation of sisal fabric resulted in an increase of  $T_g$ . This is attributed to the

lowering of mobility of the rubber-fabric system. It can also be seen that  $T_g$  values decrease to lower temperatures upon chemical treatment. This decrease is due to the ineffective interfacial bonding which enhances the mobility of the molecular chains resulting in the transition state being pushed to lower limits.

### 3.1.3 Frequency dependence of textile composites

The mechanical behavior of viscoelastic materials is dependent on time (or frequency) as well as on temperature. The variation of dynamic properties of sisal fiber reinforced polypropylene with frequency has been investigated by Joseph et al.<sup>9</sup>. The authors observed that storage modulus increased with frequency and this increase was prominent at higher temperatures. Figures 7 and 8 represent the variation of storage modulus of the untreated and thermally treated composites with temperature at three different frequencies 0.1, 1 and 10 Hz. It can be clearly seen that storage modulus increases with frequency and this increase is prominent only at low temperatures. This can be attributed to the lesser mobility of the rubber chains when the speed of cyclic stress is too fast to bring about deformation.

### 3.2 Thermogravimetric analysis

Generally it has been seen that the incorporation of plant fibers into different matrices increases the thermal stability of the system. In an interesting study the thermogravimetric analysis of biodegradable composites comprising of poly(Propylene carbonate)(PPC) and short, lignocellulose fiber *Hildegardia populifolia* was performed by Li et al.<sup>10</sup> and the investigation revealed that the introduction of the fiber led to a slightly improved thermo-oxidative stability of PPC.

However anomalous results were noticed in some other natural fiber reinforced composites. The thermal properties of several lignocellulosic fiber reinforced polyester composites was investigated by Hassan and Nada.<sup>11</sup> The fibers used were rice, straw, bagasse and cotton stalk. They observed that all the lignocellulosic fiber reinforced polyester composites were slightly thermally less stable than the neat polyester

composite. The thermal properties of rubberwood fiber-thermoplastic natural rubber composites was determined by Sameni et al.<sup>12</sup> The authors observed an increasing degradation temperature of the samples with rubber-wood fiber.

The TG and derivative (DTG) thermograms of the untreated and treated sisal fabric reinforced rubber composites are shown in Figures 9 & 10. Table IV gives the peak temperatures and % weight loss of the various composites. For the gum composite, the peak at 360.5°C corresponds to the maximum degradation of rubber matrix. In the case of the composite containing woven sisal fabric, the peak temperatures have decreased to 329.3 °C and a new peak has come at 480.2 °C due to hemicellulose and  $\alpha$ -cellulose degradation. For the composite containing fabric treated with bonding agents and alkali the peak temperatures have increased to 501.3°C ad 501.7° C. This means that mercerization has resulted in greater thermal stability for the composites. For the composites containing silane treated sisal fabric it can be seen that the peak temperatures have shifted to temperatures 487.2 °C and 482.5°C indicating that silane treated composites are thermally less stable than alkali treated composites. Thermal stability is found to be maximum for the composite containing the thermally treated sisal fabric which is evident from the peak temperature at 504°C. The amount of residual char left after 600°C increases for the composite containing alkali treated sisal fabric. A similar observation was reported by Ray et al.<sup>13</sup> for alkali treated jute fibers who explained that mercerization reduced the hemicellulose to a considerable extent giving rise to a lignin-cellulose complex thereby making the product more stable than the raw sample and this was reflected in the increased amount of char left behind.

## CONCLUSIONS

An investigation into the viscoelastic properties with thermal resistance and morphology of woven sisal fabric reinforced natural rubber composites is presented. Storage modulus was found to increase upon reinforcement of natural rubber with sisal fabric. This was attributed to the increase of stiffness to the rubber-fabric network. Chemical modification of sisal fabric resulted in lowering of storage modulus. This is due to the partial unwinding and loosening of individual fiber strands disrupting the alignment of yarns in

the warp and weft directions. The damping parameter registered a decrease upon chemical modification due to lowering of mobility of the polymer chains. Storage modulus was also found to increase with frequency for the untreated as well as the treated composites. Thermogravimetric analysis revealed that composites containing chemically treated fabric were thermally more stable than untreated composite and among the composites containing chemically treated fabric, thermally treated composites were found to be more stable. This was substantiated in the increase of decomposition temperatures of hemicelluloses and  $\alpha$ -cellulose for the treated composites. Morphologically, it was noticed that there was a poor adhesion in alkali treated composites as the alkali was unable to penetrate into the thick sisal fabric.

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**CAPTIONS TO FIGURES**

1. Weave pattern of sisal fabric.
2. Schematic sketch of sisal fabric – natural rubber composite
3. Variation of storage modulus with temperature as a function of chemical modification.
4. Scanning electron micrographs of tensile fracture surfaces of chemically modified textile composites (a) composite containing untreated sisal fabric [Untreated] (b) composite with bonding agent [Bonding agent] (c) composite containing alkali treated fabric [4% NaOH] (d) composite containing aminosilane treated fabric [A1100] (e) composite containing methyl silane treated fabric [A174] (f) composite containing thermally treated fabric [Thermal].
5. Variation of loss modulus with temperature as a function of chemical modification.
6. Variation of damping factor with temperature as a function of chemical modification
7. Variation of storage modulus of the untreated composite with temperature at different frequencies.
8. Variation of storage modulus of the thermally treated composite with temperature at different frequencies
9. TG thermograms of the composites.
10. DTG thermograms of the composites.

**Reference:**

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- <sup>1</sup> Kuzak, S.G.; Shanmugam, A.; J. Appl. Polym. Sci. 73, 649, **1999**
  - <sup>2</sup> O'Donnell, A.; Dweib, M.A.; Wool, R.P.; Composites Science and Technology 64, 1135, **2004**
  - <sup>3</sup> Aziz, S.H.; Ansell, M.P.; Composites Science and Technology 64, 1219,2004
  - <sup>4</sup> Aziz, S.H.; Ansell, M.P.; Composites Science and Technology 64, 1231, 2004
  - <sup>5</sup> Guigo, N.; Vincent, L.; Mija, A.; Naegele, H.; Sbirrazzuoli, N.; Composites Science and Technology 69,1979,2009
  - <sup>6</sup> Bledzki, A.K.; Jaszkievicz, A.; Scherzer, D.; Composites Part A 40,404,2009
  - <sup>7</sup> Jacob, M.; Thomas, S.; Varughese, K.T.; Polymer Composites 27, 671,2006
  - <sup>8</sup> Jacob, M.; Thomas, S.; Varughese, K.T.; Composites Science & Technology 64, 955, 2004
  - <sup>9</sup> Joseph, P.V.; Mathew, G.; Joseph, K.; Groeninckx, G.; Thomas, S.; Composites Part A 34, 275, 2003
  - <sup>10</sup> Li, X.H.; Meng, Y.Z.; Wang, S.J.; Rajulu, A.V.; Tjong, S.C.; J. of Polymer Science Part B - Polymer Physics 42, 666, 2004
  - <sup>11</sup> Hassan, M.L.; Nada, A.M.A.; J. of Appl. Polym. Sci. 87, 653, 2003
  - <sup>12</sup> Sameni, J.K.; Ahmad, S.H.; Zakaria, S.; Polymer - Plastics Technology and Engineering 42, 139-152, 2003
  - <sup>13</sup> Ray, D.; Sarkar, B.K.; Basak, R.K.; Rana, A.K.; J. of Appl. Polym. Sci. 85, 2594, 2002

*Table I*

Properties of sisal fabric

Properties of sisal fabric	
Yarn distance (weft)	3 mm
Yarn distance (warp)	5 mm
Twist (turns per mm)	10
Areal density (g/m <sup>2</sup> )	1500

Table II

Ingredients	Gum	T	TB	TBA	TBAS	TBMS	TT
NR	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Resorcinol	-	-	7.5	7.5	7.5	7.5	7.5
Hexa	-	-	4.8	4.8	4.8	4.8	4.8
TDQ <sup>a</sup>	1	1	1	1	1	1	1
CBS <sup>b</sup>	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Sisal fabric	-	✓	✓	✓	✓	✓	✓
Treatment	-	-	-	4% NaOH 1 hr	Amino- silane	Methyl silane	Heat

a- 2,2,4 trimethyl-1,2-dihydro quinoline

b- N-cyclohexylbenzothiazyl sulphenamide

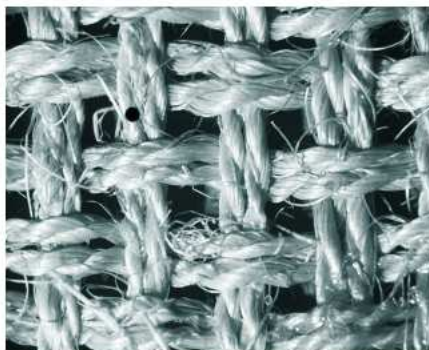


Table III

Sample	$T_g$ [°C]	
	E'' peak	Tan delta peak
Gum	-54	-50
T	-45	-48
T B	-55	-58
TBA	-52	-55
TBAS	-50	-53
TBMS	-52	-55
TT	-52	-56

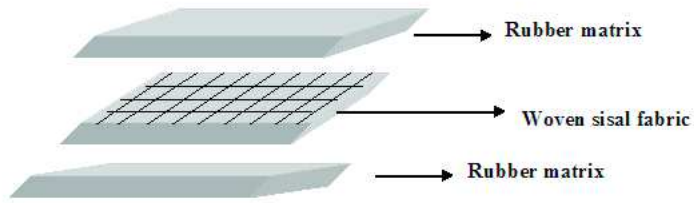
*Table IV*

Samples	Temperatures °C		% Weight at 700°C
	Peak I	Peak II	
Gum	360.5	-	3.2
T	329.3	480.2	3.4
TB	355.8	501.3	3.6
TBA	357.9	501.7	5.4
TBAS	353.0	487.2	3.3
TBMS	348.9	482.5	3.9
TT	360.0	504.0	3.5

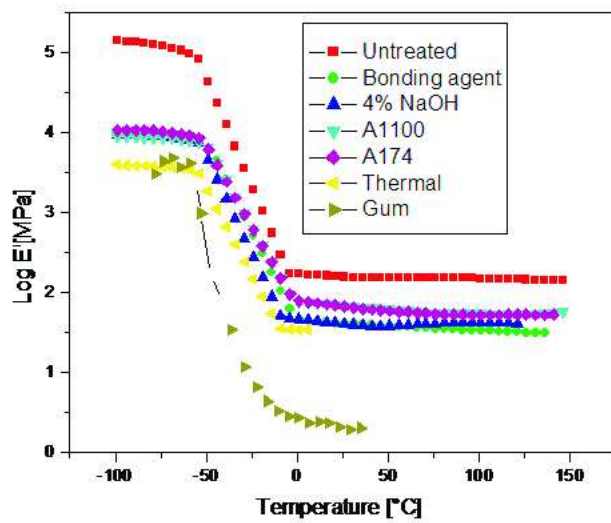


**Figure 1**

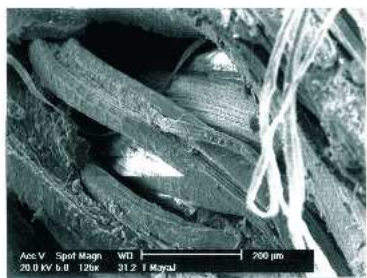
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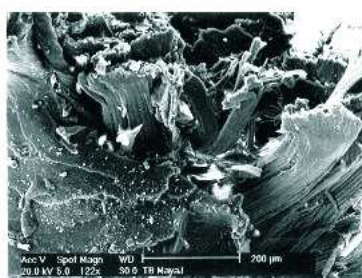
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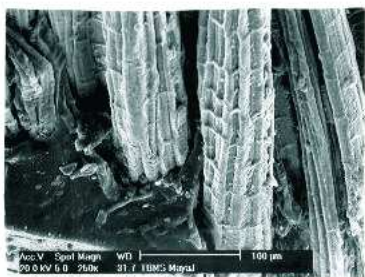
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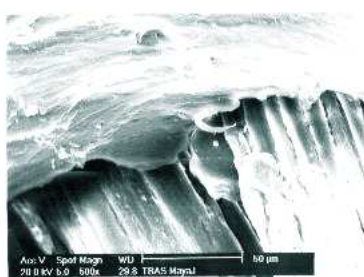
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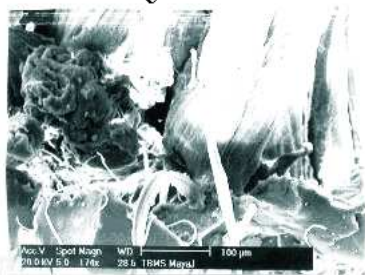
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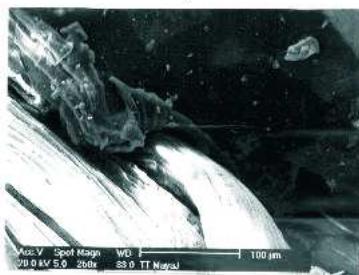
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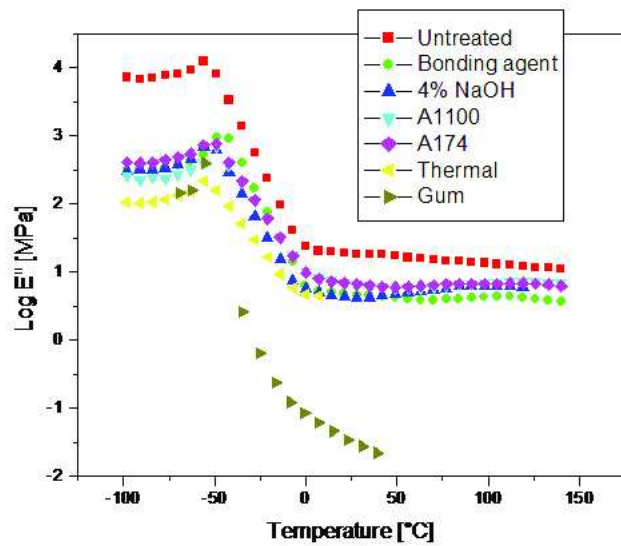
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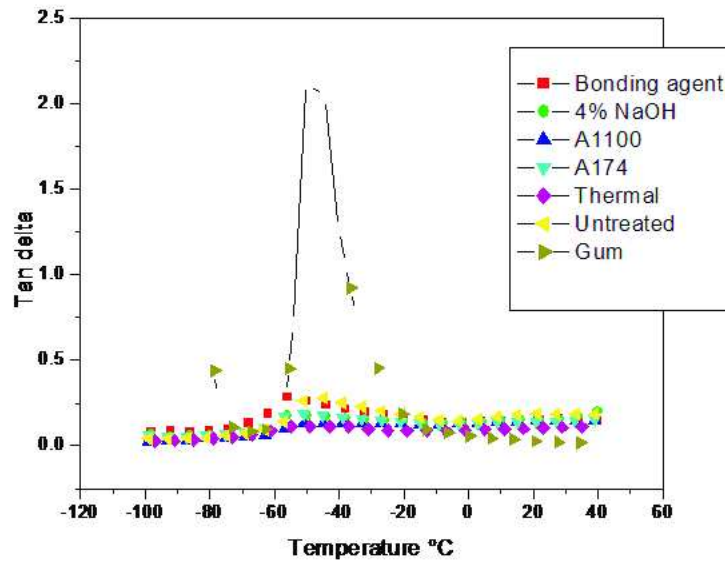


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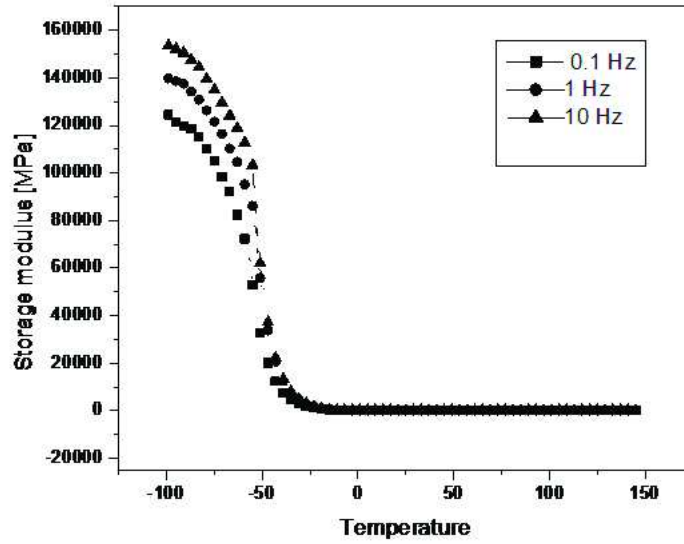
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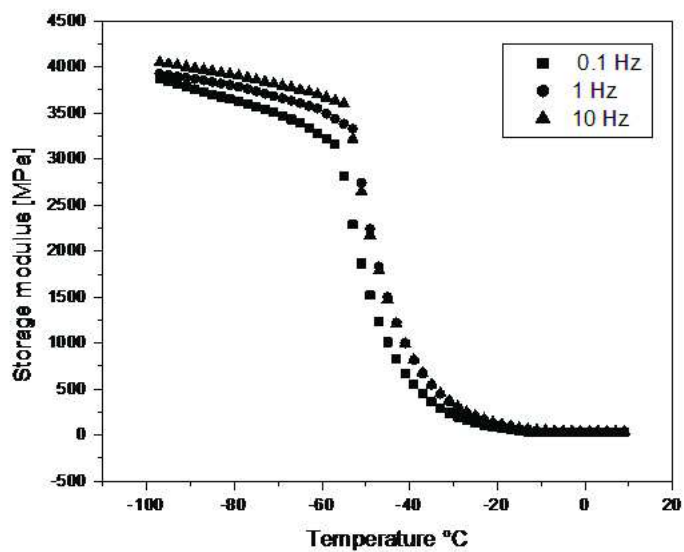


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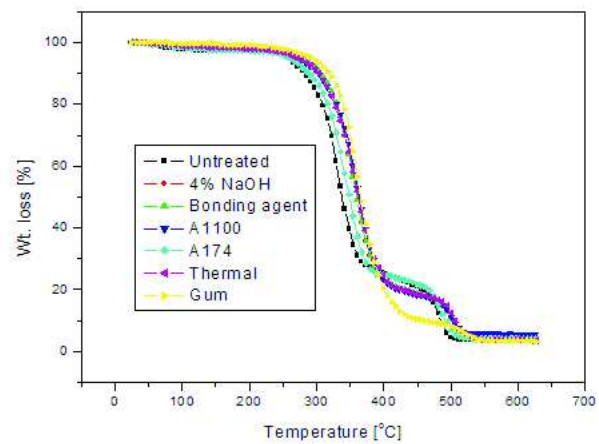




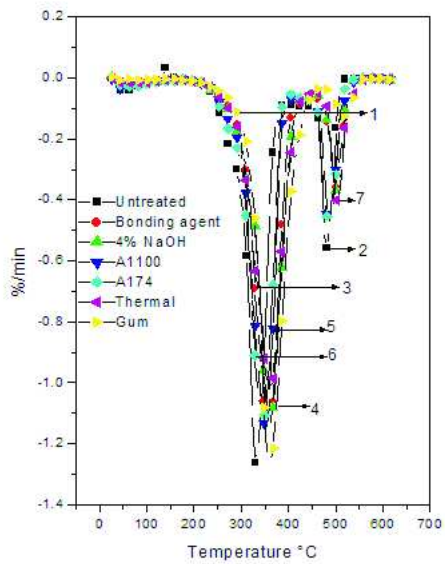
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